U.S. Patent Application Serial No.: 10/540,833
Request for Reconsideration Under 37 C.F.R. 1.116 filed February 19, 2010
Response to Official Action dated October 19, 2009

REMARKS

The Official Action dated October 19, 2009 has been carefully considered. Accordingly, the present response is believed sufficient to place the present application in condition for allowance. Reconsideration is respectfully requested.

Claims 5, 7, 10-13 and 18 were rejected under 35 U.S.C. 102(b) as being unpatentable over Miyahara et al, U.S. Patent No. 5,840,830. The Examiner asserted that Miyahara et al teach that sodium sulfide can be produced by in situ reaction of sodium hydrosulfide and sodium hydroxide (column 4, lines 61-64), that these reactants can be used in equimolar amounts (column 6, lines 49-53) and therefore in the claimed molar ratio range of 0.95-1.02, and that, if such a step is employed, the resulting ratio of total number of moles of NaOH to charged sulfur source is (23.45/22.83) or 1.027, whereby Miyahara et al anticipate the process of claim 5.

This rejection is traversed and reconsideration is respectfully requested. Applicants submit that Miyahara et al do not teach the process of claim 5 or the improvements thereof in providing poly(arylene sulfide) (PAS) with an improved combination of properties. More particularly, Miyahara et al do not teach the process for producing a PAS according to the present invention and as defined in claim 5 wherein (1) the dehydration step employs the alkali metal hydroxide in a proportion of 0.95 to 1.02 mol per mol of the alkali metal hydrosulfide, or (2) the total number of moles of (i) alkali metal hydroxide formed with hydrogen sulfide formed upon the dehydration, (ii) alkali metal hydroxide added prior to the dehydration, and (iii) alkali metal hydroxide added after the dehydration, per mol of charged sulfur source is in the range 1.015 to 1.050. As will be set forth in detail below, the calculations provided in the Official Action to support the rejection have been carefully examined and are believed to conflict with

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the actual teachings of Miyahara et al. Further, when the teachings of Miyahara et al are correctly used to calculate the molar ratio of the alkali metal hydroxide to the alkali metal hydrosulfide in the dehydration step and to calculate the total number of moles of alkali metal hydroxide per mol of charged sulfur source, it is evident that Miyahara et al do not anticipate the process of claim 5 or claims 7, 10-13 and 18 dependent thereon.

The process of claim 5 comprises four important process steps which, in combination, provide a PAS having a desirable combination of improved properties as also set forth in claim 5. Specifically, in the dehydration step (1), an alkali metal hydrosulfide and an alkali metal hydroxide, both as aqueous mixtures, are heated and reacted in an organic amide solvent in a proportion of 0.95 to 1.02 mol of alkali metal hydroxide per mol of the alkali metal hydrosulfide, wherein distillate containing water is discharged to the exterior of the system and hydrogen sulfide formed upon the dehydration is discharged as a gas to the exterior of the system. As the discharge of hydrogen sulfide to the exterior of the system is directly linked with a weight loss of sulfur amount in the system, it is evident that the discharged hydrogen sulfide is not recycled into the reaction system.

In the Official Action, the Examiner asserted that since Miyahara et al teach that sodium sulfide can be produced by in situ reaction of sodium hydrosulfide and sodium hydroxide (column 4, lines 61-64), and that these reactants can be used in equimolar amounts (column 6, lines 49-53), the claimed molar ratio range of 0.95-1.02 is met. Applicants submit, however, that even if the sodium sulfide exemplified by Miyahara et al is replaced by equimolar amounts of sodium hydrosulfide (NaSH) and sodium hydroxide (NaOH), the molar ratio required in the

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dehydration step (1) of claim 1 is not met. The teachings of Miyahara et al are carefully reviewed to determine the NaOH/NaSH molar ratio.

Miyahara et al's moles of alkali metal hydrosulfide

More specifically, Miyahara et al describe that Example 1a was conducted in the same manner as Comparative Example 1a with respect to the amount of sodium sulfide, wherein "3,800 g of sodium sulfide pentahydrate containing 46.20 wt. % of sodium sulfide (Na_2S)" (column 10, lines 58-59) was employed. The number of moles of sodium sulfide is therefore (3,800 x 0.4620)/78.05 = 22.49 moles, as the molecular weight of sodium sulfide is 78.05. The 22.49 moles of sodium sulfide used by Miyahara et al is confirmed by the Miyahara et al disclosure that after dehydration, the NMP solution in the gas absorber was recycled to the reaction vessel and "As a result, the amount of the available sulfur existing in the reaction vessel was recovered to 22.39 mol. Therefore, loss of H_2S was 0.44 mol % of the charged amount of Na_2S" (column 12, lines 37-39). Thus, the initial amount of Na_2S is 22.39/(1-0.0044) = 22.39/0.9956 = 22.49 mol.

The Official Action incorrectly asserts that the loss of H_2S was 0.44 **mol**, rather than the 0.44 **mol** % disclosed at column 12, lines 37-39 of Miyahara et al. The actual loss of H_2S is 22.49 mol x 0.0044 = 0.1 mol, which corresponds to the 0.1 mol loss described at column 12, lines 27-29: "The distillate collected in the three-necked flask contained 1,454 g of water and 0.1 mol (25% of the whole H_2S vaporized off) of H_2S (containing substantially 0 g of NMP)."

Assuming that the alkali metal hydrosulfide and the alkali metal hydroxide are used in an equimolar amount in Example 1a of Miyahara et al, as asserted in the Official Action, the 22.49 mol of sodium sulfide is equivalent to 22.49 mol of the alkali metal hydrosulfide and 22.49 mol

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of the alkali metal hydroxide. Thus, 22.49 mol of alkali metal hydrosulfide NaSH is used in such a method.

Miyahara et al's moles of alkali metal hydroxide

As noted, the alkali metal hydrosulfide and the alkali metal hydroxide are used in an equimolar amount in Example 1a of Miyahara et al, whereby the 22.49 mol of sodium sulfide is equivalent to 22.49 mol of the alkali metal hydrosulfide NaSH and 22.49 mol of the alkali metal hydroxide NaOH. Miyahara et al further describe that Example 1a was conducted in the same manner as in Comparative Example 1a except that a different reaction apparatus was used, 30 g of 97% NaOH were added to the 20-liter autoclave, and the charged amount of NMP was changed from 6,000 g to 5,000 g, thereby performing dehydration over 3.5 hours (column 12, lines 16-21). Thus, Miyahara et al also add 30 g of 97% NaOH, or $(30 \times 0.97)/40.0 = 0.73$ moles NaOH, as 40.0 is the molecular weight of sodium hydroxide.

The Official Action incorrectly asserts that Applicants' calculations improperly include the amount of additional NaOH added after the dehydration step. However, Miyahara et al clearly indicate that the 30 g of 97% NaOH were added and dehydration was performed (column 12, lines 16-21), and, in contrast, Miyahara et al disclose that an additional 7.9 g of 97% NaOH is added after the dehydration step (column 12, lines 34-46). The 7.9 g is not included in the present calculation.

Thus, 22.49 mol NaOH + 0.73 mol NaOH, or 23.22 mol NaOH is used in such a method.

Miyahara et al's molar ratio of alkali metal hydroxide to the alkali metal hydrosulfide

The Miyahara et al molar ratio of alkali metal hydroxide to the alkali metal hydrosulfide is therefore 23.22 mol NaOH / 22.49 mol NaSH = 1.032. The Miyahara et al molar ratio in the

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dehydration step is therefore outside the range of 0.95 to 1.02 recited in step (1) of the process of claim 5.

Examples 1b, 2 and 5 of Miyahara et al employ NaOH/NaSH amounts and molar ratios similar to those of Example 1a. In Example 3a, the equimolar amounts of alkali metal hydrosulfide and alkali metal hydroxide are 21.28 mol each. Miyahara et al disclose the addition of 30 g of 97% NaOH (0.73 mol NaOH) for the dehydration step, not after dehydration as asserted in the Official Action. Thus, Example 3a employs a molar NaOH/NaSH ratio of (21.28 + 0.73)/21.28, which is equal to 1.034. Example 3b of Miyahara et al is similar to Example 3a. In Example 4a, the equimolar amounts of alkali metal hydrosulfide and alkali metal hydroxide are 21.28 mol each, and Miyahara et al disclose the addition of 50 g of 97% NaOH (1.21 mol) for the dehydration step, not after dehydration as asserted in the Official Action, resulting in a molar NaOH/NaSH ratio of (21.28 + 1.21)/21.28, which is equal to 1.057. Example 4b of Miyahara et al is similar to Example 4a. Thus, according to the teachings of Miyahara et al, the NaOH/NaSH ratio is above the upper limit of 1.02 required in step (1) of the process of claim 5.

In the subsequent charging step (2) of claim 5, the total number of mols of (i) alkali metal hydroxide formed with hydrogen sulfide upon the dehydration, (ii) alkali metal hydroxide added prior to the dehydration, and (iii) alkali metal hydroxide added after the dehydration is 1.015 to 1.050 mols per mol of the charged sulfur source and the mols of water are controlled to provide 0.5 to 2.0 mols of water per mol of the charged sulfur source. The amount of the charged sulfur source is calculated out in accordance with the equation: [Charged sulfur source] = [Total moles of sulfur charged] – [Moles of sulfur volatized out after dehydration].

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In the Official Action, the Examiner asserted that Miyahara et al teach in Example 1a a ratio of total number of moles of NaOH to moles of charged sulfur source of (23.45/22.83) or 1.027 (pages 5-6). Applicants submit, however, that the calculations in the Official Action are incorrect and that the molar ratio of total NaOH to charged sulfur source required in step (2) of claim 1 is not met by Miyahara et al.

<u>Miyahara et al's moles of charged sulfur source</u>

Claim 5 defines the "Charged sulfur source" as "Total moles of sulfur charged" less "Moles of sulfur volatilized out after dehydration." Miyahara et al describe that after dehydration, the NMP solution in the gas absorber was recycled to the reaction vessel and "As a result, the amount of the available sulfur existing in the reaction vessel was recovered to 22.39 mol" (column 12, lines 37-38). As described above, this is consistent with the 0.1 mol loss described at column 12, lines 27-29 from the originally charged 22.49 mol. Thus, the charged sulfur source is 22.39 mol, whether as sodium sulfide or as alkali metal hydrosulfide.

<u>Miyahara et al's moles of total NaOH</u>

Claim 5 defines the total moles of NaOH as "the total number of moles of (i) an alkali metal hydroxide formed with hydrogen sulfide formed upon the dehydration, (ii) the alkali metal hydroxide added prior to the dehydration, and (iii) the alkali metal hydroxide added after the dehydration."

1. <u>Moles formed with hydrogen sulfide formed upon the dehydration</u>

As described above, the actual loss of H_2S is 22.49 mol x 0.0044 = 0.1 mol, which corresponds to the 0.1 mol loss described at column 12, lines 27-29 of Miyahara et al: "The distillate collected in the three-necked flask contained 1,454 g of water and 0.1 mol (25% of the

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whole H_2S vaporized off) of H_2S (containing substantially 0 g of NMP)." The NaOH formed

during the H_2S formation calculated according to the following equation:

$$Na_2S + 2H_2O \rightarrow H_2S + 2NaOH.$$
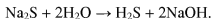
Thus, the moles of (i) an alkali metal hydroxide formed with 0.1 mol hydrogen sulfide formed

upon the dehydration is 0.2 mol NaOH.

2.   Moles added prior to the dehydration

As noted above, if the alkali metal hydrosulfide and the alkali metal hydroxide are used

in an equimolar amount in Example 1a of Miyahara et al, the 22.49 mol of sodium sulfide is

equivalent to 22.49 mol of the alkali metal hydrosulfide NaSH and 22.49 mol of the alkali metal

hydroxide NaOH. Additionally, Miyahara et al describe that Example 1a was conducted in the

same manner as in Comparative Example 1a except that a different reaction apparatus was used,

30 g of 97% NaOH were added to the 20-liter autoclave, and the charged amount of NMP was

changed from 6,000 g to 5,000 g, thereby performing dehydration over 3.5 hours (column 12,

lines 16-21). Thus, Miyahara et al also add 30 g of 97% NaOH, or $(30 \times 0.97)/40.0 = 0.73$ moles

NaOH, as 40.0 is the molecular weight of sodium hydroxide. Thus, the moles of (ii) an alkali

metal hydroxide added prior to the dehydration is 22.49 mol NaOH + 0.73 mol NaOH, or 23.22

mol NaOH.

3.   Moles added after the dehydration

Miyahara et al describe in Example 1a that "the amount of additional NaOH added after

the dehydration step" as "7.9 g of 97% NaOH" (column 12, line 45). This corresponds to 0.19

mol NaOH, $(7.9 \times 0.97)/40$, as the molecular weight of sodium hydroxide is 40. Thus, the moles

of (iii) the alkali metal hydroxide added after the dehydration is 0.19 mol NaOH.

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4.   Total moles of NaOH

The total moles of NaOH is therefore 0.2 mol NaOH + 23.22 mol NaOH + 0.19 mol

NaOH, or 23.61 mol NaOH.

Miyahara et al's molar ratio of total NaOH to charged sulfur source

The molar ratio is therefore 23.61 mol total NaOH / 22.39 mole charged sulfur source =

1.054. The Miyahara et al molar ratio after the dehydration step is therefore outside the range of

1.015 to 1.050 required in step (2) in the process of claim 5.

Examples 1b and 2 of Miyahara et al employ similar amounts of total NaOH and charged

sulfur source and therefore the molar ratios in step (2) are similar to those of Example 1a. In

Example 3a, the equimolar amounts of alkali metal hydrosulfide and alkali metal hydroxide are

21.28 mol each, the charged sulfur source is 21.18 mol, and the total NaOH is 22.34 mol (21.28

mol charged + 0.73 mol added for dehydration + 0.2 mol from H_2S formation + 0.13 mol added

after dehydration), resulting in a total NaOH/charged sulfur source molar ratio of 1.055.

Example 3b of Miyahara et al is similar to Example 3a. In Example 4a, the equimolar amounts

of alkali metal hydrosulfide and alkali metal hydroxide are 21.28 mol each, the charged sulfur

source is 21.18 mol, and the total NaOH is 22.84 mol (21.28 mol charged + 1.21 mol added for

dehydration + 0.2 mol from H_2S formation + 0.15 mol added after dehydration), resulting in a

total NaOH/charged sulfur source molar ratio of 1.078. Example 4b of Miyahara et al is similar

to Example 4a. In Example 5, the equimolar amounts of alkali metal hydrosulfide and alkali

metal hydroxide are 22.46 mol each, the charged sulfur source is 21.96 mol, and the total NaOH

is 25.23 mol (22.46 mol charged + 0.73 mol added for dehydration + 1.0 mol from H_2S

formation + 1.04 mol added after dehydration), resulting in a total NaOH/charged sulfur source

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molar ratio of 1.149. Thus, according to the teachings of Miyahara et al, the total NaOH/charged

sulfur source molar ratio is above the upper limit of 1.050 required in step (2) of the process of

claim 5.

The present specification shows that when the NaOH/NaSH molar ratio is above 1.02, the

properties of the resulting PAS begin to decline. More specifically, in Example 3 in the

specification, wherein the NaOH/NaSH ratio is 1.04 before dehydration (comparable to that of

Example 1a of Miyahara et al), and the ratio of NaOH to charged sulfur source is 1.075, the PAS

yield is lowered, as is the melt viscosity of the PAS, while the yellow index and the amount of

dimer impurity are both increased. Thus, not only does the modification of the Miyahara et al

process to include in situ sodium sulfide formation not meet the process requirements of claim 5,

the resulting PAS exhibits a less desirable combination of properties.

Anticipation under 35 U.S.C. §102 requires that each and every element as set forth in the

claims is found, either expressly or inherently described, in a single prior art reference. *In re*

Robertson, 169 F.3d 743, 745, 49 U.S.P.Q. 2d 1949, 1950 (Fed. Cir. 1999). Miyahara et al fail

to teach a PAS production method wherein sodium sulfide is formed in situ in a dehydration step

using an NaOH/NaSH molar ratio of 0.95 to 1.02, particularly in the absence of hydrogen sulfide

gas recycling, as required by step (1) of the process of claim 5. Further, Miyahara et al fail to

teach such a process wherein the molar ratio of total NaOH to charged sulfur source is in the

range of 1.015 to 1.050, as required by step (2) in the process of claim 5. Thus, Miyahara et al

do not expressly or inherently describe each and every element as set forth in claim 5.

Accordingly, Miyahara et al do not anticipate claim 5, or any of claims 7, 10-13 and 18

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dependant on claim 5, under 35 U.S.C. §102. The rejection has therefore been overcome and

reconsideration is respectfully requested.

Claim 17 was rejected under 35 U.S.C. §103(a) as unpatentable over Miyahara et al. The

Examiner asserted that Miyahara et al render obvious the claimed melt viscosity range in

teaching that the polymerization time and temperature may be longer than what is exemplified,

and increasing the time or temperature would be expected to increase the final melt viscosity of

the PAS.

This rejection is traversed and reconsideration is respectfully requested. As claim 17

depends from, and includes all the limitations of, claim 5, the process of claim 17 is similarly

distinguishable from Miyahara et al for the reasons set forth in detail above. Moreover, the

differences between the processes of claim 17, and claim 5 from which it depends, and the

teachings of Miyahara et al are not obvious over the teachings of Miyahara et al, and one of

ordinary skill in the art would have had no apparent reason to modify the teachings of Miyahara

et al along the lines of the presently claimed process.

As set forth in the present specification, an object of the present invention is to provide a

production process for a PAS which is extremely low in content of bis(4-chlorophenyl) sulfide, a

dimer impurity produced in the polymerization reaction. It is also an object to produce as PAS

which has excellent reactivity to silane coupling agents such as γ-aminopropyl-triethoxysilane

(i.e., aminosilane), has low volatile matter, and is good in color tone, and to produce such a PAS

by use of an alkali metal hydrosulfide and an alkali metal hydroxide as these reactants are less

expensive than the traditionally employed alkali metal sulfide, in a stable polymerization

reaction. Claim 5 accordingly defines the process as producing a PAS having a bis(4-

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chlorophenyl) sulfide content lower than 30 ppm as determined by a gas chromatographic

analysis, a melt viscosity value (MV1) of 30 to 500 Pa·s as measured at a temperature of 310°C,

and a shear rate of 1,216 sec^{-1}, a ratio (MV2/MV1) of a melt viscosity value (MV2) of the

poly(arylene sulfide) after a reaction with aminosilane to the melt viscosity value (MV1) before

the reaction of 2.1 to 3.0 as measured at a temperature of 310°C and a shear rate of 1,216 sec^{-1},

and a yellow index of at most 7. With the bis(4-chlorophenyl) sulfide dimer content lower than

30 ppm, the concentration of chlorine as a functional group at the ends of the polymer chains is

reduced, whereby reactivity between a polymer end and a silane is improved. As a result, a

coupling reaction between polymer chains readily occurs through the silane reaction and a

polymer having a high melt viscosity as recited in claim 5 can be achieved, wherein the ratio

(MV2/MV1) is 2.1 to 3.0.

The fact that the use of an alkali metal hydrosulfide as a sulfur source is known is

recognized by the present inventors in the present specification. However, use of such reactants

in a stable process to produce a PAS, particularly a PAS having the properties recited in claim 5,

has not been known. As noted in the specification, beginning at page 2, line 17, it has been

difficult to set conditions for stably performing the polymerization reaction, and inhibition of

side reactions has been difficult, the volatile matter content in PAS products has been great, and

the reduction of the content of the bis(4-chlorophenyl) sulfide impurity has been difficult.

On the other hand, according to the production process recited in claim 5, not only is a

stable reaction provided, but side reactions resulting in unwanted impurities are inhibited.

Although the reaction mechanism is not fully elucidated, the reason why a stable reaction is

provided and undesirable reactions are minimized in the process of claim 5 has been

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investigated. While not wishing to be bound by theory, the following three main reactions are considered to occur in the dehydration step using NaSH.

$$NaSH + NaOH \rightarrow Na_2S + H_2O \qquad (a)$$

$$Na_2S + 2H_2O \rightarrow H_2S + 2NaOH \qquad (b)$$

$$NaSH + H_2O \rightarrow H_2S + NaOH \qquad (c)$$

These three reactions are considered to be in a delicate equilibrium state which is believed to affect the subsequent polymerization step and the equilibrium state is maintained by the conditions recited in step (1) of claim 5. Miyahara et al do not recognize or disclose any such equilibrium state resulting from use of NaSH and, in particular, Miyahara et al do not describe reaction (c), $NaSH + H_2O \rightarrow H_2S + NaOH$, or recognize its effect on a dehydration step employing NaSH and NaOH. As a result, not only do Miyahara et al not disclose the limitations of claim 5 as noted above, Miyahara et al provide no apparent reason to modify the dehydration step, particularly to employ the alkali metal hydroxide in a proportion of 0.95 to 1.02 mol per mol of the alkali metal hydrosulfide as recited in step (1), or to conduct the polymerization step (2) using 1.015 to 1.050 total moles of NaOH per mol of a sulfur source as recited in claim 5. Thus, Miyahara et al provide no apparent reason to modify the dehydration step to provide a stable reaction and/or to inhibit the undesirable side reactions.

These are critical differences between the teachings of Miyahara et al and the process of the present invention as Applicants have discovered that the in situ formation of sodium sulfide from an alkali metal hydrosulfide and an alkali metal hydroxide in the dehydration reaction requires careful control to reliably provide a PAS having a desirable combination of properties. Miyahara et al do not teach the careful control that is necessary and, in fact, the processes

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exemplified by Miyahara et al, if modified to include the in situ formation of sodium sulfide, do not result in the process of claim 5, or claim 17 is depending therefrom.

Accordingly, the process of claim 17 is nonobvious over and patentably distinguishable from Miyahara et al, whereby the rejection under 35 U.S.C. §103 has been overcome. Reconsideration is respectfully requested.

It is believed that the above represents a complete response to the Official Action and places the present application in condition for allowance. Reconsideration and an early allowance are requested.

Please charge any fees required in connection with the present communication, or credit any overpayment, to Deposit Account No. 503915.

Respectfully submitted,

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